

Edited by Shinzo Yamashita and Tosuke Kaneko, Handbook of crosslinkers
 First Edition, Taiseisha Co., Ltd., October 20, 1981 (20.10.81), page 18 left
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 to 13

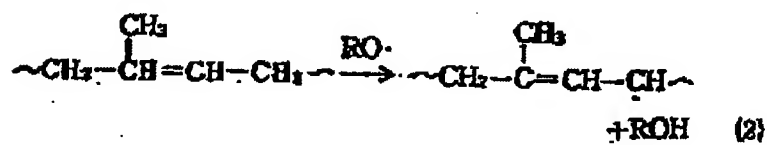
3.2 Reaction with an unsaturated polymer

A radical forming by decomposition of organic peroxides effects various reactions depending on the structure of an unsaturated polymer. Elementary reactions thereof are summarized as follows:

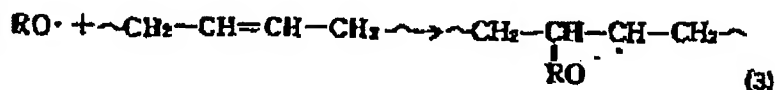
(i) Decomposition of a peroxide



(ii) Hydrogen pull reaction of an initiator radical (initiation reaction)

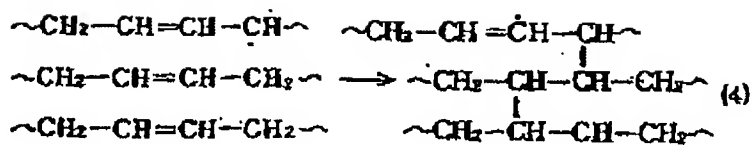


(iii) Addition reaction of an initiator radical (initiation reaction) ^{3,4)}



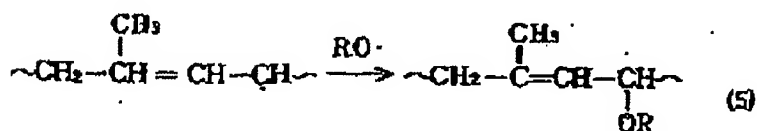
In cis-1,4-polyisoprene, the reaction of formula (2) prevails over the reaction of formula (3).

(iv) Chain addition reaction of a polymer radical to a double bond (growth reaction)



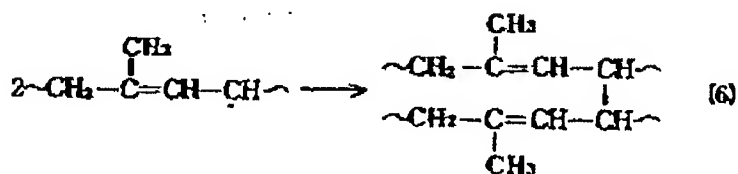
This reaction is prone to occur in 1,4-polybutadiene, especially in 1,2-polybutadiene (in addition, see formula 8).

(v) Addition reaction of an initiator radical to a polymer radical (non-crosslinking type termination reaction)



This reaction is prone to occur when benzoyl peroxide (BPO) is used⁵⁾. This is also considered as one reason why the heat resistance of a BPO crosslinked diene type rubber is poor.

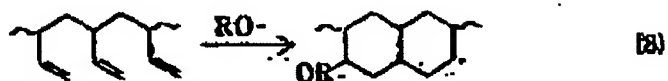
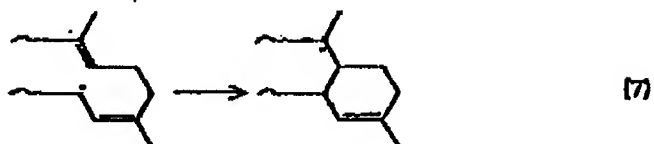
(vi) Coupling reaction between polymer radicals (crosslink type termination reaction)



As intermolecular crosslinking reactions, there are two types of formulae (4) and (6). When cis-1,4-polyisoprene is crosslinked with dicumyl peroxide, the reaction of formula (6) dominates⁶⁻⁸⁾. On the other hand, in polybutadiene, a chain addition reaction of formula (4) occurs^{9,10)}. Therefore, the crosslinking efficiency of peroxides (see 3.3) is higher in the latter. As the reasons thereof, the steric hinderance of methyl group in 1,4-polyisoprene and the stability of 1,4-polyisoprene radical by hyperconjugation can be considered.

(vii) Cyclization reaction of a polymer radical

(intramolecular migration reaction)

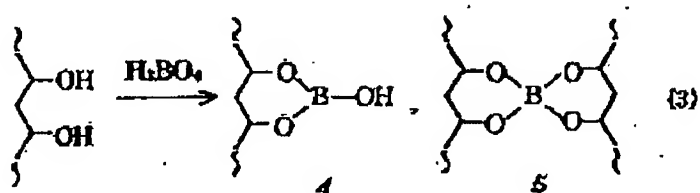


It is reported that the cyclization reaction of formula (8) also occurs depending on a reaction condition⁴⁾. In 1,2-polybutadiene, the reaction is especially prone to occur¹¹⁾.

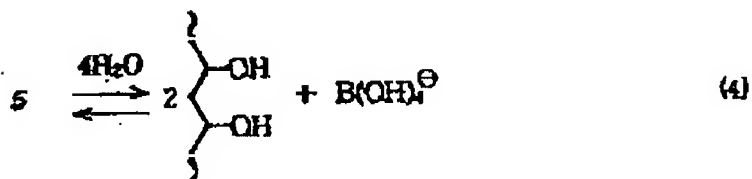
As to the crosslinkings against unsaturated polyesters and diallyl phthalates by organic peroxides, see III-9 and V-2.

14.2 Crosslinking by boric acid

Polyvinyl alcohol (PVA) affords the product of 4 in the dilute solution of boric acid, whereas, in the concentrated solution, crosslinked product of 5 is obtained²⁾.



The crosslinking point of borate crosslinked PVA gel 5 is dissociated by elevation of temperature (formula 4)³⁾.



The activation energy necessary for the dissociation of the crosslinking point is 6 kcal/mol³⁾.